Optimisation of Waste Vegetable Oil-Based Thermoset Polymers

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Abstract

Bio-based thermoset polymers were produced from epoxidized waste vegetable oils cured with anhydrides at different molar ratios. Properties were compared to analogues produced with neat oil and DGEBA as a feedstock. Thermal stability proved to be affected by the molar ratio, and the use of feedstock from waste oil resulted in no effect on this property. DMA has shown that higher concentrations of anhydride enhance the storage modulus, T_g (up to 42.5 °C) and crosslink density. The frying process proved to play a minor role in tuning the dynamic-mechanical properties. However, the contribution of the anhydride demonstrated to be significant enough to mitigate the losses caused by the waste oil, as shown statistically in a DOE

study. All formulations were chemically resistant to aqueous, organic and acidic media. The identification of the effects of critical parameters on the properties of WVO-based thermosets enables further production of polymers from waste streams.

1. Introduction

Bio-based epoxy polymers have been explored in different areas as an environmentally-friendly alternative for diglycidyl ether of bisphenol A (DGEBA).[1–3] Despite the versatility, performance and dominance in the epoxy market, DGEBA is directly derived from bisphenol A (also known as BPA), which in turn is linked to a series of serious health hazards.[4–6] In this regard, epoxidized vegetable oils (EVO) have been extensively applied in epoxy formulations due to the advantages associated with the exploration of vegetable oils, such as renewability, abundance and chemical versatility.[7] EVO can be used either as a reactive diluent or solely as a source of polymerisable epoxy groups, significantly increasing the renewable content, reducing the environmental impact and providing novel properties to these systems.[2,8–10] Nevertheless, there are challenges associated with the reduced performance of EVOs and economic disadvantage that hinder the full industrial production of these materials at a competitive level versus DGEBA.[11,12] Additionally, some studies question that the exploitation of edible vegetable oils may negatively affect the security of the food supply-chain in a long-term.[13–15]

In this scenario the use of waste vegetable oils (WVO) previously used in deep frying emerges as an opportunity to explore a bio-based but non-edible source of triglycerides to produce epoxy polymers and polymers in a more sustainable fashion. The technological exploration of WVO is intrinsically aligned with the concepts of sustainability as it can promote economic, environmental and sociological valorisation of this material.[16–20] Also, from a life cycle assessment perspective, WVO can be considered a burden-free starting material since the environmental impacts associated with the cultivation and use-phase (deep-frying process) can be omitted in the production of chemicals from food waste.[21]

In previous studies, our group demonstrated the successful utilisation of epoxidized WVO as reactive diluent for DGEBA formulations to produce blends with increased bio-based content.[22] Prior to the epoxidation step, purification methodologies were applied to remove by-products formed during the use-phase that are responsible for altering the physical and chemical properties of the oil.[23,24] Therefore, epoxy polymers produced from purified WVO performed similarly to analogous obtained from neat oil when mixed with DGEBA. These formulations were subsequently used to successfully produce composites with recycled carbon fibre with high tensile performance.

Although the previous investigations produced polymers and composites with satisfactory performance, these systems still present DGEBA as the major component in the formulation, consequently compromising the environmental performance. Therefore, in the present work we investigate the production of bio-based thermoset polymers formed exclusively with epoxy polymers derived from WVO (*i.e.* absence of DGEBA) and cured with different cyclic anhydrides. Despite the popularity of amine hardeners, EVO-based systems are cured more effectively with anhydrides due to their increased chemical affinity with electron-rich oxirane rings.[25] These investigations systematically inspected parameters in the thermoset formulation such as hardener type, the molar ratio between epoxy groups and hardener and the curing catalyst to understand and optimise the thermal, chemical and dynamic-mechanical properties of the resulting polymers. Moreover, these formulations were compared with analogous produced from neat VO to assess the impact in performance caused by replacing the edible triglycerides by waste materials and with DGEBA formulations to compare the performance of the materials produced in this study against a benchmark material.

2. Materials and Methods

2.1 General Considerations

Waste vegetable oil (used in deep fry medium for four days, blend of rapeseed/palm oil approximately 3:1, WVO) and neat vegetable oil (NVO) were collected from a food outlet at University of Warwick, Coventry, UK. Hydrogen peroxide (30 % v/v), toluene (puriss. p.a. >99.7 %), dichloromethane (puriss. 99%), phthalic anhydride (PA, 99%), methyl-hexahydrophtalic anhydride (MHHPA, 96 %, mixture of isomers cis and trans) and 2-methylimidazole (2-MI, 99 %) were supplied by Sigma-Aldrich. $MgSO_4$ (dried), triethylamine (TEA, 99 %) and H_2SO_4 (solution, 1 M) were supplied by VWR International. All chemicals, except the WVO, were used as received.

Characterization of the starting materials was performed by infrared spectroscopy in attenuated total reflection mode (ATR-FTIR) and ^{1}H Nuclear Magnetic Resonance (^{1}H NRM). ATR-FTIR (Cary Tensor 27) spectra were obtained in a range of 4000–500 cm^{-1}, accumulating 32 scans with a resolution of 4 cm^{-1}. ^{1}H NMR spectra (Bruker spectrometers HD Avance III 300 MHz and Bruker Avance III 400 MHz, operating at 300.129 MHz and 400.046 MHz, respectively), were obtained from samples of approximately 0.2 g dissolved in 500 µl of $CDCl_3$ with tetramethylsilane (Sigma-Aldrich, UK).

2.2 Synthesis of WVO-based polymers

For the synthesis of the epoxy polymers, WVO (100 mL, 1.2×10^{-1} mol, 2.5×10^{-1} mol of double bonds, 1 equivalent) purified according to procedure previously developed in the group was added to a round bottom flask containing Amberlyst 15® (22 wt%), toluene (50 mL, 50 vol%) and acetic acid (7.0 mL, 1.2×10^{-1} mol, 0.5 equivalent). After mixing the solution for 10 min at 60 °C, H_2O_2 (30% v/v, 58 mL, 5.0×10^{-1} mol, 2 equivalent) was added dropwise to the mixture over a period of 30 min and the reaction was left for 6 h under these conditions. The resulting material was filtered and the crude oil was washed with a solution of 5 wt% NaHCO3 and 5 wt% NaCl to remove acid residues. The product was dried over $MgSO_4$ for 30 min, then filtered for the removal of the drying agent. Solvent excess was extracted using a rotary evaporator.[22,26] The product obtained was a yellow oil (70% yield). The same procedure was repeated for the NVO, with the number of equivalents adjusted according to the values of degree of unsaturation determined by ^{1}H NMR.

Dynamic mechanical analysis (DMA, Triton Tritec Dynamic Mechanical Thermal Analyser) was performed using a dual cantilever bending setup with an oscillating frequency of 1.0 Hz, displacement of 0.05 mm from -60 to 100 °C at a heating rate of 2 °C min^{-1}. Specimens were in the rectangular form of a nominal size of 1.5 x 5 x 24 mm. Glass transition temperature (T_g) was defined from tanδ versus temperature as the maximum of the tanδ peak. Weight-loss curves were measured by thermogravimetric analysis (TGA) using a Mettler Toledo TGA 1 STAR^e System programmed to heat the samples from 25 to 600 °C, heating rate of 10 °C min^{-1}, under an N_2 flow of 100 mL min^{-1}. The temperature of initial degradation (T_{Onset}) was defined from the onset of the degradation temperature of the major thermal event and temperature of maximum degradation (T_{Max}) was determined from the curve of the first derivative of weight loss with respect to temperature. Chemical resistance test was performed by immersing samples of approximately 1 g in vials containing 20 ml of water, NaOH (1 M), H_2SO_4 (1 M) and toluene. These vials were kept at room temperature for 7 days, and changes in the weight and physical aspects were calculated for each pair of formulation/solution.

2.3 Preparation of thermoset polymers

Bio-based epoxy polymers were produced and characterised from purified waste vegetable oil (PVO) and NVO according to procedures published previously.[22] Approximately 10 g of bio-based epoxy polymer, (epoxidized purified vegetable oil or epoxidized neat vegetable oil, EPVO or ENVO respectively) were added to a round bottom flask, then a certain amount of hardener was added to the system. Hardener to epoxy polymer ratio was varied from 0.8:1.0 to 1.4:1.0, producing polymer systems given in Table 1. Heating (140 °C) was employed to ensure phthalic anhydride solubilisation, while MHHPA was added to

the system at room temperature since it is liquid at normal conditions. In sequence, 3 mol % (in relation to the epoxy amount) of the curing catalyst (triethylamine or 2-methylimidazole) were added to the flask. The mixture was kept under stirring for 3 minutes to ensure homogeneity, and then the solution was transferred to silicone moulds. The formulations were placed in an oven (Vacuum Oven Fistreem) at 140 °C for 16 h, and the resulting thermoset polymers were post-cured at 160 °C for 2 h. The full description of the formulations is presented in Table 1

3. Results and Discussions

3.1 General Considerations

The study was designed to assess differences in the performance of bio-based thermoset polymers produced from waste oil-based epoxy polymers and analogous materials from conventional vegetable oil. Therefore, this comparison permits the identification of the effect of the oil use phase (frying process) in the properties of the resulting polymers, as well as understand how to maximise the performance of these systems. Figure 1 summarises the preparation steps of the thermoset polymers, from the purification of the WVO (leading to the formation of PVO) to the curing with cyclic anhydrides. Features such as the unsaturation degree of NVO and PVO (2.88 and 2.18, respectively), as well as the number of epoxy rings per triglyceride unit (2.66 and 2.08, respectively), were defined by ^{1}H NMR. Although these oils present a lower degree of unsaturation in comparison to other VO used for the production of epoxy polymers (*e.g.* linseed oil – 6.6 double bonds per triglyceride), these blends of rapeseed/palm are a more realistic representation of oils commonly used for cooking worldwide.[27,28]

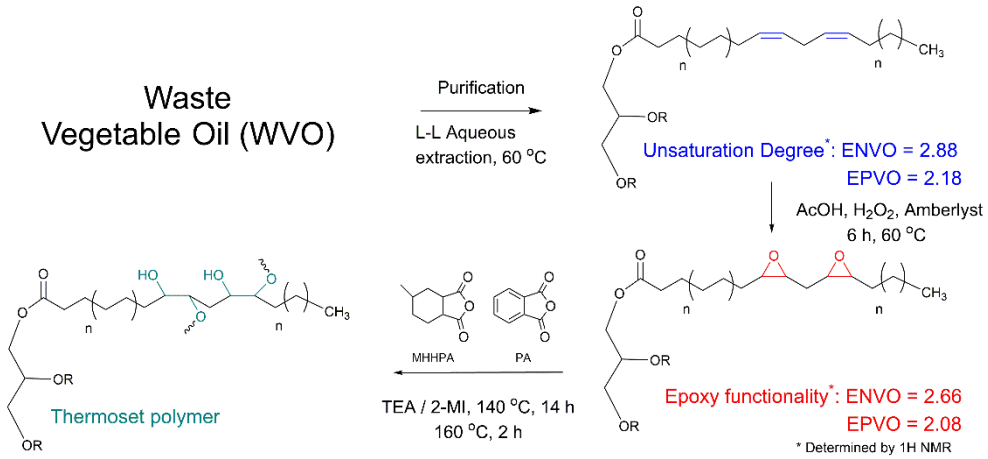

Figure 1: Production of bio-based thermoset polymers from waste vegetable oil.

3.2 Thermal stability of the bio-based polymers

The exceptional thermal stability of thermosets is one of the main characteristics that differentiate them from thermoplastics and is crucial for some of their unique applications. Therefore, it is imperative to compare the thermal degradation behaviour of bio-based polymers from WVO with those observed for neat oil and commercial DGEBA polymer samples. Thermal stability was evaluated through the mass-loss events detected in the thermogravimetric curves (from 25 to 600 °C), Figures 2A and B. Despite previous studies showing that the thermal decomposition of EVO-based polymers can occur in a single-step, formulations investigated in this study presented a two-stage decomposition, with a minor and major event.[29,30] The first thermal event, observed at approximately 215 °C, corresponded to the thermal decomposition of low-molecular-weight molecules that are unincorporated into the network, *i.e.* unreacted curing agents. These events coincided with the thermal decomposition of the curing agents (213.9 and 230.6 °C for PA and MHHPA, respectively). The following weight-loss event observed at *circa* 310 °C represented the major degradation step. This phenomenon is related to the combined thermal decomposition of triglycerides and the anhydride moieties, which consequently led to the destruction of the network integrity. This behaviour is commonly observed for thermosets produced from EVO and was evidenced by TGA/FTIR/GCMS studies carried by Tan et al.[31,32]

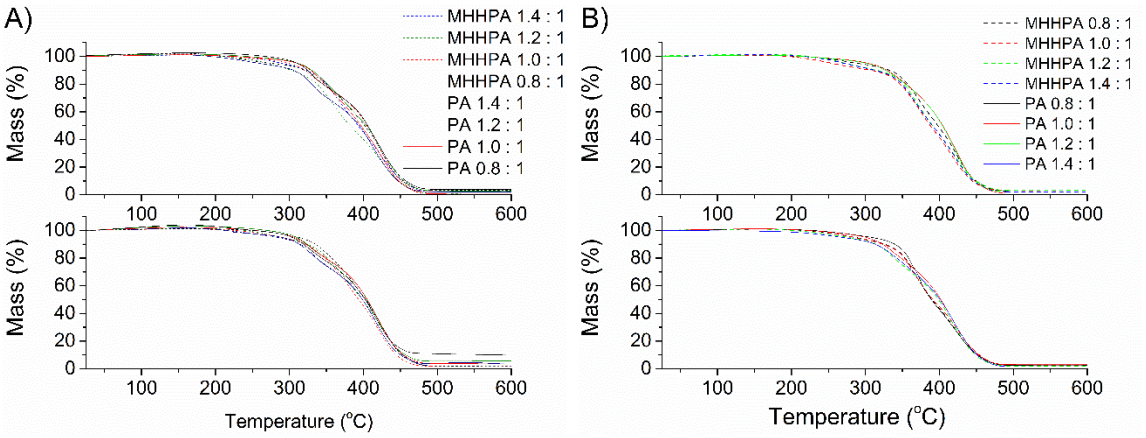

Figure 2: Thermograms of the polymers from formulations: A) ENVO-based (top) and EPVO-based (bottom) catalysed with TEA and B), ENVO-based (top) and EPVO-based (bottom) catalysed with 2-MI, from 25 °C to 600 °C, under N_2 atmosphere.

Table 2 presents the values of T_{Onset} and T_{Max} for all thermoset formulations and for the constituents that originated the polymers. The anhydride content, given by the molar ratio, proved to be the main agent that

influences this property, and networks richer in anhydride demonstrated to have reduced thermal stability. This can be seen as a consequence of the reduced thermal stability of the anhydride moiety in comparison with the triglycerides moiety.[22] In other words, the network becomes more abundant in the less thermally-stable component, thereby degrading at reduced temperatures. Moreover, the minor degradation event observed at lower temperatures became increasingly more significant at higher molar ratios, meaning that a more substantial proportion of unreacted anhydrides that were not incorporated into the network.

The strategy of replacing neat oil with WVO in the formulations demonstrated to cause no significant effect regarding the thermal stability of the thermosets since T_{Onset} and T_{Max} presented no relationship with the origin of the polymer. This observation is aligned with previous reports that revealed that there is no direct connection between the degree of functionality of EVO and the thermal stability of the resulting thermosets.[31] The choice of the curing catalyst also demonstrated no particular tendency as both sets of formulations behaved similarly.

3.3 Dynamic Mechanical Properties

Dynamic mechanical analyses (DMA) were performed to determine the viscoelastic response and the mechanical properties of the bio-based polymers in a range of temperature. Figure 3A and B show the curves of storage modulus versus temperature of compositions catalysed with TEA (T_ENVO and T_EPVO series) and with 2-MI (MI_ENVO and MI_EPVO series), respectively. These curves revealed the dependence of the maximum storage modulus (E′) with the hardener molar ratio and with the anhydride selection. Anhydride-rich formulations (high molar ratio) produced polymers with superior E′ as consequence of the superior molecular rigidity of the hardeners in comparison to the aliphatic backbone of the EVOs. Consequently, the more hardener in the formulation, the stiffer is the polymer network. In addition, EVO-rich polymers reached the rubbery plateau at lower temperatures in comparison to anhydride-rich formulations, demonstrating the effect of the mobility gain provided by the aliphatic moieties. These findings illustrate the ability of control of the polymer properties according to the hardener: epoxy molar ratio balance

Regarding the effect of the selection of the hardener in the properties, formulations produced with PA presented higher storage modulus in comparison to MHHPA. This result is a consequence of the superior rigidity of the PA molecular structure, which displays an aromatic structure, versus the cycloaliphatic backbone found in MHHPA. No relationship regarding the oil origin and the initial E′ could be derived as values were similar. Nevertheless, formulations presented more prominent differences when E′ is analysed at 25 °C (consider as a working temperature). ENVO-based polymers presented superior E`(25 °C) versus

EPVO analogous, demonstrating that temperature is an important factor when comparing both sets of polymers since it interferes with the chain mobility.

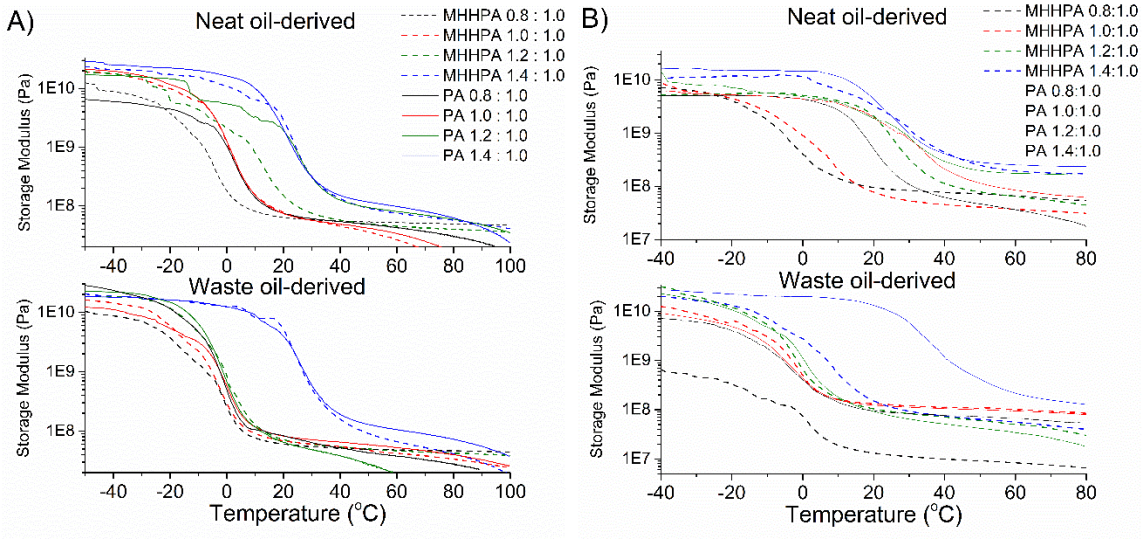

Figure 3: Curves of storage modulus versus temperature for polymers produced with A) TEA and B) 2-MI as catalyst. Top curves derive from neat oil-based polymers and bottom curves from waste oil-based polymers.

To further understand changes in the mechanical properties of these thermosets with the temperature variation and the differences between the ENVO and EPVO-based formulations, the glass transition temperature (T_g) of the polymers was investigated and calculated from the maximum peak of tanδ curves (Figure 4A and B). Values for T_g are presented in Table 3. Although the T_g could have been inferred from dynamic DSC runs, this transition was not clearly defined in the thermograms since this relaxation occurred in a broad range of temperatures, therefore not providing a precise value for the transition. On the other hand, DMA data provided a direct measure of the transition due to chain mobility gain, and the use of the maximum of the tanδ peak enabled a clearer identification of the T_g.

Results revealed a strong dependence of the T_g with the combination of parameters covered in this study (hardener, molar ratio, oil source and catalyst), ranging from -3.4 to 42.5 °C. These values, although smaller in comparison to the commercial DGEBA formulation used as internal standard (SuperSap CLR®, 56.3 °C), are comparable to similar polyester thermosets produced from EVO reported in the literature (from -8 to 65 °C).[30] All curves presented broad tanδ peaks, which is characteristic for the relaxation of

heterogeneous networks.[33] In the context of EVO-based thermosets, this observation is a consequence of the distribution of oxirane groups across the triglyceride backbone, which produces a statistical distribution of double bonds since the starting materials derive from mixed triglycerides.[34]

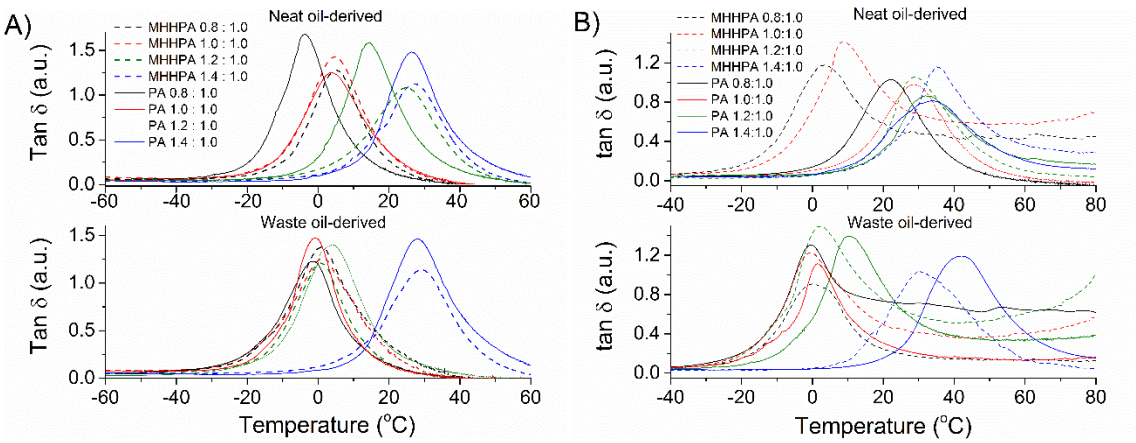

Figure 4: Curves of tanδ versus temperature for polymers produced with A) TEA and B) 2-MI as catalyst. Top curves derive from neat oil-based polymers and bottom curves from waste oil-based polymers.

Tanδ curves revealed that formulations with increased anhydride molar ratio resulted in polymers with higher T_g, therefore attenuating the contribution of the aliphatic chains towards an overall increase in the network mobility. Furthermore, chain flexibility played an important role at lower anhydride ratio levels: unreacted aliphatic chains provoked act as plasticisers, consequently further reducing the T_g of the systems.[31] The combination of both effects caused the final mechanical response to be the sum of the contributions of hardener rigidity and the plasticising effect; therefore, the T_g values presented a non-linear increase with the anhydride molar ratio.

The use of polymers from WVO (formulations T_EPVO and MI_EPVO) led to polymers with T_g that generally were smaller than the analogous from neat oil (formulations T_ENVO and MI_ENVO) as consequence of the reduced number of oxirane rings per triglyceride unit as previously discussed. Therefore, it can be seen that these polymers have a less tightly interconnected network between the epoxy and anhydride moieties and, consequently, presented increased capacity of gaining coordinated mobility. Previous studies demonstrated that EVOs rich in unsaturated bonds (linseed oil, for example) produces polymers with increased T_g when compared to less unsaturated oils, which is due to the formation of a higher crosslink density.[35] Moreover, these findings explain differences observed for E` (25 °C). Dynamic-mechanical curves revealed no secondary transitions (*e.g.* T_β) were identifiable at the low-temperature end of the tanδ curve. Discrepancies observed in polymers resulting in a few formulations (T_EPVO_MHHPA

1.4:1, T_EPVO_PA 0.8:1 and T_EPVO_PA 1.4:1), where the T_gs was superior to analogous produced from ENVO, can be attributed both to the broad nature of the transition, which makes the definition of a precise value challenging and to the combination of the plasticising effect previously discussed.

The crosslink density (ν_e), property which is also directly linked to characteristics such as hardness, impact strength and brittleness of thermoset polymers, was calculated for all formulations through the relationship described by Equation 1 and presented in Table 3.[30] In this expression, E' is the storage modulus at a given temperature, R is the universal gas constant ($8{,}314\times10^3$ cm^3 MPa K^{-1} mol^{-1}) and T is the temperature of the rubbery plateau, described as (T_g+40) K. This expression permits further understand how the degree of functionality and the mechanical properties of the thermosets are related. Values of ν_e demonstrate that the increase in molar ratio led to a denser network on all systems as a consequence of a higher availability of crosslinking units, meeting previous observations about the relationship between ν_e and hardener molar ratio.[36]

Equation 1 $$\nu_e = \frac{E`}{3RT}$$

Polymers produced from WVO presented smaller values of ν_e when compared to analogues produced from ENVO, which supports the hypothesis that polymers produced from waste vegetable oil have fewer crosslinks due to the lower functionality of the polymer. In addition, thermosets cured with 2-MI as catalyst presented higher ν_e than those produced from TEA, corroborating the superior values of T_g previously observed for series MI_ENVO and MI_EPVO in comparison to T_ENVO and T_EPVO Differences caused by using these catalysts are a consequence of the higher catalytic activity of imidazoles compared with tertiary amines in the initiation step, therefore facilitating the creation of the network.[37] The increase of the anhydride ratio also led to the increase of ν_e in all formulations, confirming that tighter networks were formed in the presence of a stoichiometric excess of the hardener.

A Design of Experiment (DOE) approach was utilised to investigate the effects of experimental parameters on the resulting T_g and to calculate the significance of each experimental factor and the secondary interactions. This permitted classifying each parameter according to its contribution towards increasing the T_g of the polymers, therefore providing insights for future studies. The T_g was chosen for this particular analysis due to the importance of this property in terms of defining real-life applications for polymeric materials. A 2^4 factorial experiment was built from the 32 formulations, according to the positive and negative levels presented in Table 4. To build a symmetric factorial, the four levels of anhydride molar ratio were clustered as into low (non-stoichiometric and stoichiometric levels, 0.8:1.0 and 1.0:1.0) and high (stoichiometric excess, 1.4:1.0 and 1.2:1.0) levels. The T_g response was analysed in Minitab 17 (Minitab

Ltd, UK) using a stepwise analysis to produce a DOE model containing factors over a 95 % confidence interval.

The Pareto chart (Figure 5) demonstrates that the molar ratio (factor C) is the most statistically significant parameter in regulating the T_g of these polymers, whereas the choice of catalyst (factor D) and the oil origin (factor A) have smaller contributions passing the significance error bar at 2.048. Figure 5 also presents the main effects plots; however, interactions plots are suppressed since they demonstrated no statistical effect on the T_g. The increase in T_g caused by the high level of m[1]olar ratio is explained by the combination of increased stiffness of the anhydride and a higher crosslink density previously observed in these formulations.

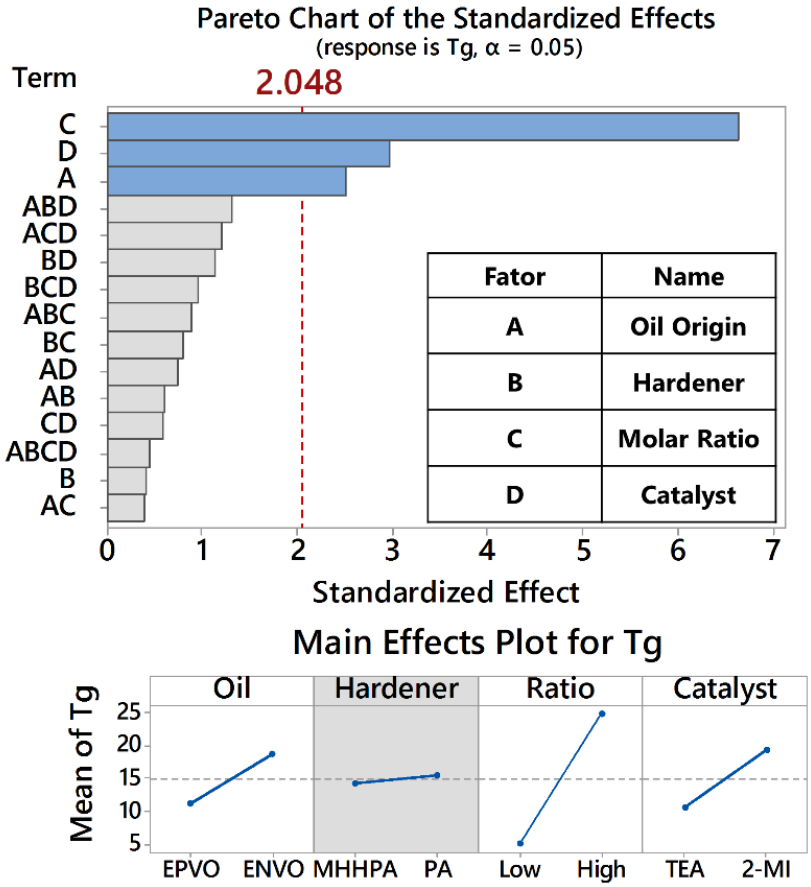

Figure 5: Pareto charts and main effects plot for standardised experimental conditions for the T_g of bio-based epoxies. Grayed out factors represent removed factors due to a significance valve lower than 95%.

Therefore, this statistical test demonstrated that the increase in T_g caused by using high contents of anhydride is significant enough to mitigate the reduction in this property caused by the reduced functionality

of WVO-based polymers. The DOE also confirmed the importance of the choice of curing catalyst since the increased reactivity of 2-MI led to polymers with superior T_g. Interestingly, the selection of hardener (factor B) proved to have no significant impact on the T_g despite hardeners causing differences observed in the storage modulus curves. DMA studies demonstrated that despite the compromise in mechanical properties of the thermoset produced by the reduced functionality of WVO-based polymers in comparison to neat oil, other factors such as the molar ratio of the anhydride and the catalyst can be used to tune the properties of the thermosets and mitigate the losses.

3.4 Chemical Resistance

The exceptional solvent resistance of thermoset polymers derives from the tightly connected crosslinks formed during the curing process, and this characteristic is responsible for defining several applications for these systems in areas such as coatings and sealers. To comprehend the effect of the incorporation of WVO-based polymers in this property, the chemical resistance of polymers produced in this study was evaluated according to their relative resistance in water, NaOH (1 M), H_2SO_4 (1 M) and toluene. As schematically presented in Table 5 all formulations showed remarkable stability in aqueous and acidic media as no significant changes were observed either in volume, weight or physical aspect. Samples immersed in toluene swelled with weight gains ranging between five and seven times the initial weight. Nevertheless, no samples were completed dissolved in this medium. Precise volume changes were not recorded since the samples' dimension changed irregularly.

Despite the resistance in the previous conditions, the formulations behaved differently in NaOH: some polymers swelled after immersion for seven days while the same conditions led to the complete dissolution of some other group of formulations. This variation in responses is similar to those previously reported for bio-based epoxy polymers produced vegetable oils such as from Karanja oil and *Mesua ferrea L.* seed oil.[29,38] The particularly poor chemical resistance of EVO-based thermosets in alkali medium is a consequence of the hydrolysable ester bonds in alkali conditions, therefore deconstructing the network.[39]

In this regard, a parallel can be drawn between the chemical resistance and the ν_e. As demonstrated by Narute et al., thermosets with higher ν_e possess superior chemical resistance as denser and tighter crosslinks hinder the solvent penetration.[40] By comparing 3 and 5, it can be observed that samples are displaying crosslink density above the empirical threshold of 0.076×10^{-3} mol cm^{-3} were resistant to complete dissolution due to alkaline hydrolysis of the ester groups. Consequently, formulations produced with increased anhydride molar ratio and cured in the presence of 2-MI presented the most satisfactory performance in chemical resistance tests. In addition, this experiment demonstrated that the origin of the

bio-based epoxy polymer played no significant role in defining the chemical resistance of the polymer, therefore supporting the utilisation of WVO concerning this property.

4. Conclusions

Thermoset polymers were successfully produced by the combination of bio-based epoxy polymers prepared from waste vegetable oil with cyclic anhydrides in the presence of two different catalytic systems. This work demonstrates the first application of this material for this particular application. The comparison of these formulations with analogous to neat vegetable oil revealed that both polymers produced thermosets with similar thermal stability and chemical resistance. Differences in mechanical performance were observed as a function of the degree of functionality of EPVO polymers in comparison with EPVO equivalents. Nevertheless, a statistical analysis identified and classified the most significant parameters with regards to increasing the T_g of these polymer, demonstrating that the contribution of the anhydride molar ratio can mitigate the reduction in properties caused by the reduced functionality of the waste vegetable oil-based polymer. The inspection of other parameters revealed that 2-methylimidazole resulted in polymers with increased T_g and higher crosslink density. Furthermore, increased anhydride/epoxy molar ratio produced thermosets with superior storage modulus, but reduced thermal stability. Therefore, this study recommends the utilization of high molar ratios of anhydride and 2-methylimidazole as catalyst to enable the production of thermosets with competitive mechanical properties from waste vegetable oil. The optimisation of the formulation was necessary step to permit further studies on the quantification of the impacts of the production of these thermosets. Moreover, these findings open space for the development of a new class of bio-based epoxy polymers (and thermosets) that are more affordable, valorise a waste-stream and with minimum impact on the performance that can be applied for the production of composites.

5. Acknowledgments

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